

LiC₆ Studied by X-ray Absorption and X-ray Emission Spectroscopy

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INTRODUCTION

The electronic structure of Li-intercalated graphite (LiC₆) has been thoroughly investigated both experimentally [14, 5, 6, 4, 11] and theoretically [3, 8, 7, 13]. It is believed that, upon lithiation, the shape of the graphite density-of-states (DOS) remains largely unchanged and electrons are completely transferred from the Li 2s states to empty carbon π^* states. This can be understood within the framework of the so-called rigid-band model, where the in-plane part of the LiC₆ band structure is the result of backfolding of the 2D bands of graphite into the smaller Brillouin zone of LiC₆. However, due to existence of lithium ions and the altered stacking of the graphene layers, the electronic structure needs consideration of changes in the band structure beyond the rigid-band model, as shown by various experimental results [4, 5, 14].

Here we present the x-ray absorption and resonant x-ray emission spectra of LiC₆. X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) are traditionally used for studying the occupied and unoccupied density of states (DOS) of various materials. Both spectroscopies have bulk probing ability due to comparatively large photon attenuation lengths, and orbital and symmetry selectivity by virtue of dipole selection rules. Resonant inelastic soft X-ray scattering (RIXS) of highly oriented pyrolytic graphite (HOPG) has shown the possibility to obtain symmetry-resolved band information [15, 2].

EXPERIMENTS

The experiments were performed at beamline 7.0.1 [16] of the Advanced Light Source, Lawrence Berkeley National Laboratory. A large (10×10 mm) highly oriented pyrolytic graphite (HOPG) sample, cut with the surface in the basal plane, was cleaved using adhesive tape to obtain a fresh surface prior loading it in the vacuum chamber. The LiC₆

sample was prepared, exposing a HOPG to Li vapor in a vacuum chamber, as described in paper [9]. The sample was brought to the beamline in a sealed container, and introduced into the vacuum system via a load lock with a glove bag under argon atmosphere.

The base pressure in the experimental chamber was $5 \cdot 10^{-9}$ mbar. XAS was obtained by measuring the total electron yield (TEY) from the sample as function of the incoming photon energy. All spectra were normalized to the photocurrent from a clean gold mesh introduced into the beam. The x-ray emission spectra was recorded using a high-resolution grazing-incidence grating spectrometer [12], with a resolution better than 0.3 eV. The bandpass of the exciting photon beam was set to 0.1 eV for absorption and 0.3 eV for the emission measurements.

RESULTS

Figure 1 shows the experimental spectra of LiC_6 . The spectra of HOPG are added for comparison. The upper panel shows the TEY XAS spectra and normal/non-resonant x-ray emission spectra. The XAS spectra of HOPG is fairly well understood, with the transition from C 1s to unoccupied π states around 285 eV, and the transition to unoccupied σ states at 291.6 eV. Comparing this to the spectra of LiC_6 , we find that the σ states in LiC_6 are shifted 1.3 eV towards lower energy. Inverse photoemission result of graphite and LiC_6 have shown a -1.9 eV shift of the σ bands[5]. The σ feature is much sharper in our x-ray absorption spectra compared to the inverse photoemission data. The discrepancies could be due to the effect of the core hole, which should dominate the shifting and shaping of the core-excited DOS (XAS) [1]. At the moment we are carrying out theoretical calculations to explain the shape and the shift of the σ states in the absorption spectra of LiC_6 .

The normal x-ray emission spectra were obtained using a excitation energy set well above the absorption threshold (non-resonance). Comparing the non-resonance spectrum of the two systems (HOPG and LiC_6), minor differences around 281 eV, 275 eV, and the intensity at E_F are found. The peak at 283.5 eV indicates the increased DOS at E_F in LiC_6 . Earlier published electron excited C K-emission spectra of LiC_6 also show enhancement of the x-ray emission near E_F [11]. This conclude that upon lithiation of graphite the Li 2s electrons are transferred into the carbon π bands.

Now considering the resonantly excited x-ray emission spectra, showed in the lower panel. As the energy of the incoming photon energy is changed, not much spectral change is observed for LiC_6 compared to graphite. The excitation energy dependence of graphite is understood using scattering approach[10, 2, 15]. As the momentum transfer for the photons is small, the final state electron-hole pairs must correspond to a vertical transition in k -space. The momentum of the excited electron is restricted due to the well defined excitation energy. Although the scattering approach seems to work very well for graphite, it seems like the rule of crystal momentum conservation is not valid in this case of LiC_6 . Upon lithiation the crystal structure changes moderately but it is still crystalline i.e. the insertion of lithium does not disturb the long range crystallographic order in the system and the momentum should be conserved in the scattering process as it does in graphite. It is possible that the increased DOS at E_F affects the coherence in the scattering process. For example resonant emission spectra of metals does not show

momentum conservation.

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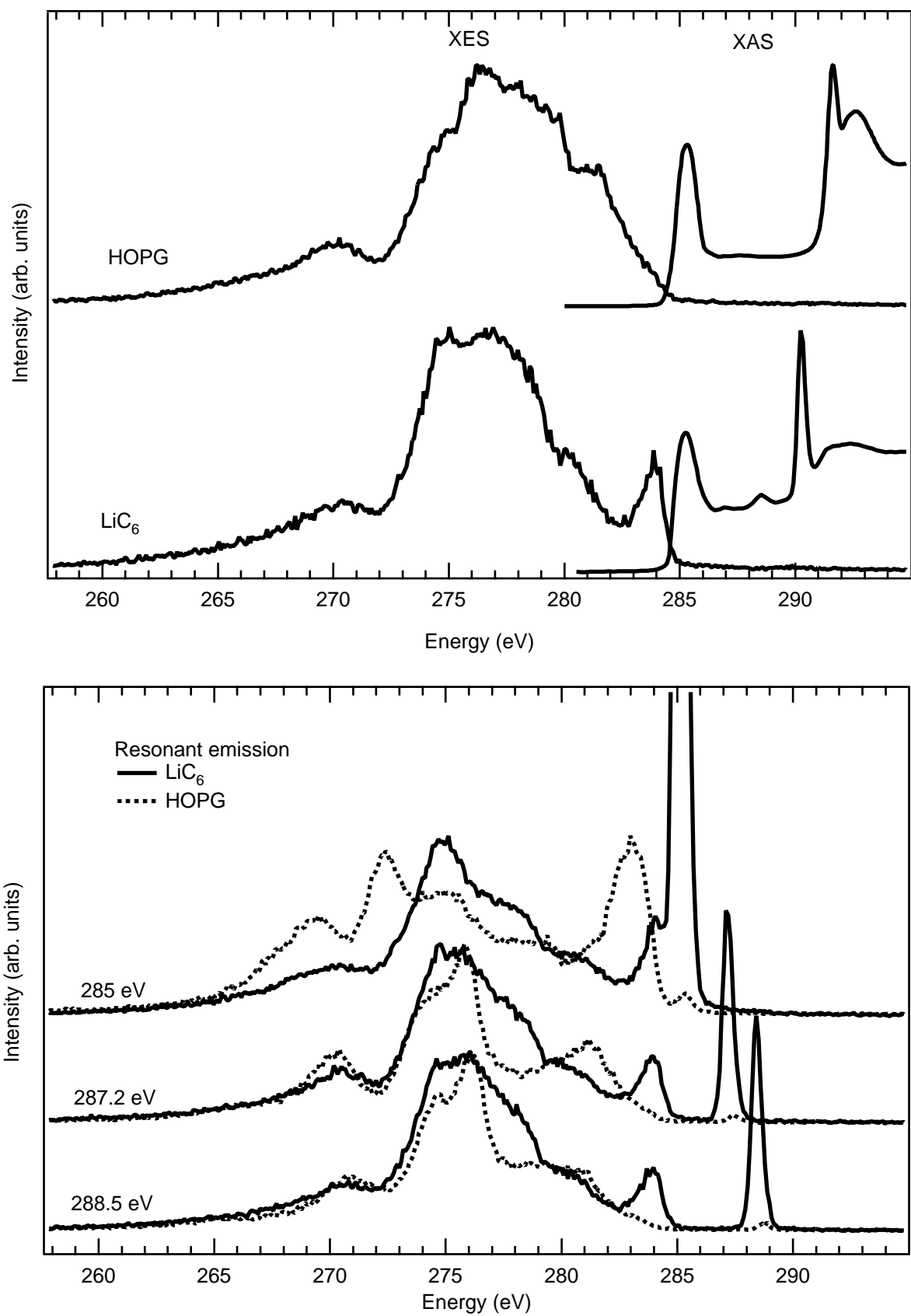


Figure 1: Upper panel, x-ray absorption spectra (TEY) and normal x-ray emission of HOPG and LiC₆. Lower panel, resonant x-ray emission spectra of HOPG and LiC₆. The used incoming photon energies are indicated.